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## Aryl Amine Antioxidant Determinations in Ester Lubricants

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<p>Many, if not all, of today's high performance lubricants, especially in jet engines, use ester basestocks inhibited with aromatic amines. Work at NRL has shown that severe and rapid depletion of the antioxidant usually precedes lubricant breakdown and subsequent mechanical failure. Therefore, an assessment of the antioxidant levels in these lubricants will serve as one measure of lubricant condition and, potentially, a lubricant's remaining lifetime. We have developed two rapid techniques to detect the most common classes of aryl amines used in today's ester lubricant formulations, the phenyl alpha-naphthylamines, diphenylamines and phenothiazines. One technique is based on a spectrochemical methodology. Here, the time evolution of the formation of an amine-indicator complex at various visible wavelengths allows the determination of phenyl alpha-naphthylamine (PAN), octylated PANs and alkylated diphenylamines. The second is based on voltammetry. The current passed through a solution of lubricant is monitored as a potential is applied to a platinum</p> <p style="text-align: right;">(Continues)</p>					
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electrode. Phenothiazines can be distinguished from the other classes of amines by its oxidation potential while concentrations can be derived from the current measurements. The latter technique is amenable to in situ measurements. Results of measurements on stressed and unstressed lubricants will be discussed. Potential applications for the two techniques, both singly and in combination, will be given.

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# ARYL AMINE ANTIOXIDANT DETERMINATIONS IN ESTER LUBRICANTS

## INTRODUCTION

Turbine engine lubricants based on trimethylol pentane (TMP) or pentaerythritol (PE) esters are widely used in both commercial and military aircraft. These lubricants undergo degradation when thermo-oxidatively stressed. To protect them, aryl amines are added to the fluid in amounts ranging from 0.5 percent to 2.0 percent by weight. The amines act as inhibitors of the radical reactions which are considered the major pathway for the ester decomposition. Ravner and Wohltjen<sup>1</sup> have shown that an ester (pentaerythritol tetrahexanoate (PETH)) protected by octylphenyl alpha-naphthylamine (O-PAN) exhibits little degradation while the concentration of the antioxidant remains above 5 percent of its initial value. However, as the antioxidant concentration approaches zero, a rapid rise in the viscosity, total acid number (TAN), and evolution of combustible gasses signifies the onset of lubricant breakdown. Similar findings were reported by Bartl and Mowery<sup>2</sup> in PAN (phenyl alpha-naphthylamine) -protected PETH. This implies, at least in oils protected by PAN and O-PAN, that monitoring the level of the antioxidant can be a measure of the lubricant's remaining lifetime. NRL has been tasked and has developed two convenient, rapid and inexpensive techniques to assess these antioxidants in ester basestocks. The tests are also sensitive to two of the other common materials used to protect esters, p,p'-dioctyldiphenylamine (DODA) and phenothiazine (PTZ).

## BACKGROUND

Attempts to assess a lubricant's remaining lifetime have been the subject of considerable interest over the past 10 years. For the analysis of new and used oils, a recent review paper<sup>3</sup> describes the use of gas chromatography, high-performance liquid chromatography (HPLC), size exclusion chromatography, IR, mass spectrometry, NMR and atomic absorption spectroscopies for solids, fuel, water, glycol and for monitoring the degradation of antioxidants and viscosity-index improvers.

Efforts have been made to assess the quality of a lubricant through its bulk properties by classical measures - acid number and viscosity, and by newer technologies such as COBRA (complete oil breakdown analyzer)<sup>4</sup>, differential thermal analysis (DTA)<sup>5</sup>, differential scanning calorimetry (DSC)<sup>6</sup>, pressure differential scanning calorimetry (PDSC)<sup>7</sup> and cyclic voltammetric analysis<sup>8</sup>. These techniques have shown some success in evaluating a lubricant's remaining lifetime, but they also suffer some drawbacks. The classical techniques have little if any predictive value. As shown by Ravner and Wohltjen<sup>1</sup>, when significant increases in viscosity or acid number are observed, lubricant breakdown is imminent. DTA, DSC and PDSC are susceptible to the presence of thermally labile contaminants such as water and fuel. The COBRA and cyclic voltammetric techniques are relatively new and the interpretation of the results of such

testing remains difficult.

An alternate method for assessing lubricant lifetime, quantifying the levels of the antioxidant(s), has also been used by several investigators. Sniegowski used thin layer chromatography (TLC)<sup>9</sup>, liquid-liquid chromatography<sup>10</sup>, and gas-liquid chromatography<sup>11</sup> to quantify PAN, PBN (phenyl beta-naphthylamine), O-PAN and DODA in gas turbine lubricants. Other workers have used gas chromatography<sup>12</sup> and reversed phase HPLC<sup>13</sup> to measure antioxidant levels. These techniques, while powerful enough to give both quantitative and qualitative information, require extensive laboratory facilities and trained technicians. As such, they would be difficult to adapt to field use or to a "quick turn-around" testing regime.

A simpler approach is to use visible absorption spectroscopy where the presence or absence of a color provides the diagnostic information on antioxidant levels. Precisely such an approach was adopted by Kauffman and Rhine<sup>14</sup>. They determined the hydroperoxide decomposing capabilities of the antioxidant in oil samples using a colored nickel complex.

A more direct technique is to use a reagent that forms a colored complex with the antioxidant. Since all the present day turbine lubricants use aryl amine antioxidants, the use of a diazonium salt is suggested. These salts are known to react with aryl amines to form highly colored azo dyes<sup>15</sup>. El Shabouri et al.<sup>16</sup> employed para-nitrobenzenediazonium sulfate for the identification of some substituted phenothiazines in drugs.

Here, the use of a para-nitrobenzenediazonium tetrafluoroborate (NBDB) as a solid, stable reagent for identifying and quantifying the antioxidants PAN, O-PAN and DODA in ester lubricants using absorption spectroscopy is reported.

Another simple technique for obtaining antioxidant levels is voltammetry using ultramicroelectrodes. A potential is applied to a solution of the species to be analyzed and the current monitored as the potential is swept positively as measured against a reference electrode. The aryl amine antioxidants will cause a dramatic increase in the current at the potential at which they undergo oxidation. This potential can be characteristic of the species being oxidized and the current will be proportional to its concentration. In non-conducting media, such as jet engine lubricants, the use of ultramicroelectrodes allows solutions of the oil in acetonitrile to be analyzed without adding supporting electrolyte. A more complete description of this analytical technique for antioxidant determination is given in a paper by Cheek and Mowery<sup>17</sup>. This report gives the results of voltammetric determinations of amine levels in unstressed jet engine lubricants and compares it with results obtained using the spectrochemical technique.

## EXPERIMENTAL

The antioxidants phenyl alpha-naphthylamine (Eastman Organic), phenothiazine (Alfa Products), octylphenyl alpha-



naphthylamine (William F. Nye, Inc.) and p,p'-dioctyldiphenylamine (William F. Nye, Inc.) were used as received. Standard solutions of the antioxidants in pentaerythritol tetrahexanoate basestock were made on a weight percent basis with the antioxidant concentration varying from 0 to 2.0. A series of test lubricant/antioxidant mixtures was also provided by the Naval Air Propulsion Center, Trenton, NJ for analysis. The series included unstressed lubricants containing known quantities of antioxidants and stressed lubricants containing unknown quantities of antioxidants.

#### A. Spectrochemical Measurements

The spectrochemical measurements were carried out on a Perkin-Elmer Lambda 5 UV/visible spectrometer using a 1 cm quartz cell fitted with a Teflon stopper. Spectrochemical analysis for the amine antioxidants was achieved by reacting basestock/antioxidant standard solutions or lubricant samples with a known concentration of para-nitrobenzenediazonium tetrafluoroborate (Pfaltz & Bauer) in reagent grade acetone (Fisher Scientific) and recording the optical density of the complexed product(s) at their absorption wavelength(s) (Fig. 1). Analyses for phenyl alpha-naphthylamine (PAN) and octylphenyl alpha-naphthylamine (O-PAN) were carried out using 2 uL of lubricant in 3.2 mL of para-nitrobenzenediazonium tetrafluoroborate (NBDB) reagent solution and with detection at

528 nm while analysis for p,p'-dioctyldiphenylamine (DODA) was carried out using 100 uL of lubricant in 3.0 mL of NBDB reagent solution and with detection at 725 nm. Analysis for phenothiazine (PTZ) was not done spectrochemically since, in lubricants, PTZ is usually found in combination with PAN and previous work<sup>2</sup> showed that PTZ and PAN form a complex in PETH. The site where the NBDB reagent binds to the PTZ is blocked in this complex and, as a result, spectrochemical analysis via the NBDB reagent is not effective. Spectrochemical detection of PTZ is possible in the absence of PAN, however.

Initially, a 0.1 percent NBDB reagent solution was used to complex the antioxidants and optical density measurements were made after a fixed time interval. Measurements for PAN or O-PAN were made 1 minute after mixing the test lubricant and the NBDB reagent and measurements for DODA were made 3 minutes after mixing. This procedure eventually evolved into one where the optical density was monitored over a ten minute interval after mixing and the reagent concentration was reduced to 0.01 percent while the original reaction volumes and detection wavelengths were unchanged.

#### B. Electrochemical Measurements

The electrochemical measurements were carried out in a cell (Fig. 2) formed from a "U"-shaped tube containing a glass frit (Ace Glass; porosity E). The cell held a 10 mm diameter platinum

ultramicroelectrode (NRL preparation) in one of its arms and a Ag/AgCl reference electrode (Bioanalytical Systems) in the other. The arm holding the ultramicroelectrode was filled with a lubricant test solution and the arm holding the reference electrode was filled with a 0.1 M NaBF<sub>4</sub> (Aldrich Chemical) aqueous electrolyte solution. A linear potential sweep was applied to the cell with a simple triangular wave potential generator (Bioanalytical Systems, Model CV-1B) and the resulting current was measured using an electrometer (Keithley, Model 610B). The potential and current outputs were recorded on a X-Y recorder (Varian, Model F-80AM).

The analytical procedure adopted involved mixing 240 L of a lubricant solution with 5.0 mL of reagent grade acetonitrile (Fisher Scientific). The acetonitrile/lubricant mixture was then introduced into the ultramicroelectrode arm of the cell and the sample volume in the cell was adjusted to a level slightly above that of the aqueous electrolyte solution. The potential was scanned from an initial value of 0.00 V to +1.50 V at a scan rate of 25 mV s<sup>-1</sup>.

## RESULTS AND DISCUSSION

### A. Spectrochemical Measurements

The spectrochemical measurements were initailly run on

standard lubricant solutions containing a single antioxidant. Using a 0.1 percent NBDB reagent solution, optical densities for complexed PAN measured at 528 nm 1 minute after mixing reagents gave a straight line that nearly passed through the origin with a slope of 0.86 and a correlation coefficient of 1.000 when plotted against antioxidant concentration (Fig.3). Similarly, a plot of optical densities for complexed O-PAN measured at 528 nm 1 minute after mixing reagents versus O-PAN concentration gave a straight line with a slope of 0.57 and a correlation coefficient of 0.992. However, the line did not pass through the origin. Optical density measurements at 725 nm for complexed DODA 3 minutes after mixing reagents gave a straight line through the origin with a slope of 0.24 and a correlation coefficient of 1.000.

While performing the spectrochemical measurements on the standard lubricant solutions, the optical densities at 528 nm were observed to increase or to decrease during the 1 minute measurement. This depended on whether the lubricant solution contained PAN or O-PAN, respectively. This occurred because the optical density for complexed O-PAN reached its maximum value immediately and was decreasing when the measurement was made. The PAN-containing lubricants, exhibiting a slower reaction rate with the NBDB reagent, were reaching their maximum optical density at the 1 minute measurement. The observation allowed distinction between PAN and O-PAN although their optical absorptions occur at nearly the same wavelength. It also accounted for the failure of the O-PAN data to pass through the

origin and for the larger standard deviations obtained for the O-PAN results.

An improvement in the accuracy and in the precision of the O-PAN measurements was made by using a 0.01 percent NBDB reagent solution and a 10 minute test interval. The more dilute solution allowed the absorbance maxima of the complexed O-PAN to be reached more gradually (2-4 minutes) and to be recorded more accurately. With the new procedure, a plot of optical density versus O-PAN concentration gave a straight line that nearly passed through the origin with a slope of 0.64 and a correlation coefficient of 1.000 (Fig.3). Use of the more dilute NBDB reagent solution did not significantly improve the accuracy of the PAN or the DODA results since the absorbance maxima of their complexed products were already reached more slowly and, thus, had been recorded accurately with the 0.1 percent NBDB.

Since the error and the variance associated with the measurements on the standard lubricant solutions with a single antioxidant appeared to be small (<5 percent) when the optimum concentration of NBDB reagent was used, the precautions taken in carrying out the measurements were assumed to be satisfactory. The precautions included using a digital timer with an alarm and mixing the test lubricant and the NBDB reagent directly in the cuvette. They also included using a cuvette with a teflon stopper to minimize evaporation of acetone from the NBDB solution and to eliminate leakage from the cuvette during mixing of the reagents. In addition, they included wiping excess lubricant

from the outside of the micropipet before delivering the sample into the reagent solution and then rinsing the micropipet several times with reagent solution to ensure delivery of the calibrated amount of test lubricant. Finally, they included recording a background optical density at the beginning and at the end of a series of optical density measurements and subtracting an average background reading from the measured reading.

Following the same procedures, standard lubricant solutions containing binary mixtures of antioxidants were analyzed using the 0.1 percent NBDB solution. At 528 nm, the measurements for PAN or O-PAN in combination with DODA and in combination with each other showed no evidence of any antioxidant interactions. However, the optical densities measured for either PAN or O-PAN in combination with PTZ were lower than expected indicating that an interaction between the antioxidants had occurred. Earlier work<sup>2</sup> showed that interaction between oxidatively stressed PAN and PTZ results in the formation of a mixed dimer; a complex of this type would be expected to hinder the reaction of the NBDB reagent.

At 725 nm, the optical densities measured for DODA in combination with either PAN or O-PAN were generally lower than expected again suggesting that some antioxidant interaction had occurred. The formation of a mixed dimer has also been demonstrated<sup>8</sup> for oxidatively stressed lubricants containing PAN and DODA. Measurements for DODA in the presence of PTZ were always higher than expected, probably due to interference by the

broad absorption of the NBDB-complexed PTZ.

Next, the unstressed lubricants (provided by The Naval Air Propulsion Center) were analyzed using the 0.1 and 0.01 percent NBDB reagents for the PAN and O-PAN determinations and the 0.1 percent NBDB reagent for the DODA determination. The results of measurements at 528 nm and at 725 nm are shown in Tables 1 and 2, respectively. As seen from the first table, the percentage of PAN or O-PAN determined by our spectrochemical procedure agrees within 10 percent of the "true" percentage except for sample 2A. This suggests that perhaps sample 2A was incorrectly formulated or that the "true" percentage cited for that sample is in error. Spectrochemical analysis also indicated that unstressed oil sample 10D-2 contained O-PAN instead of PAN. Electrochemical analysis and analyses done at NAPC confirmed this result.

Table 2 shows that large errors (10-70 percent) are associated with the determination of DODA. This was expected since most of the unstressed lubricant samples contain 2 or more antioxidants and spectrochemical measurements on the standard solutions showed that antioxidant interactions were likely.

The stressed lubricant samples were analyzed using only the 0.1 percent NBDB reagent. Results of measurements, shown in Table 3, indicate that most of the PAN and the O-PAN in these samples has been depleted while a significant quantity of DODA remains. In fact, the amount of PAN or O-PAN that is left is less than 0.1 percent in most cases and less than 0.5 percent in all cases. At these low antioxidant levels, distinction between

the PAN and O-PAN was not possible by our spectrochemical procedure.

## B. Electrochemical Measurements

The electrochemical measurements were initially performed on standard solutions of single antioxidants, as before. Figure 4 shows the cyclic voltammograms observed and the half-wave potentials measured for these standard solutions. As seen from the figure, solutions containing either PAN or PTZ give voltammograms with unique curve shapes and with unique half-wave potentials (i.e. the second wave for PTZ). In contrast, O-PAN and DODA give voltammograms that have similar shapes and half-wave potentials that are nearly identical. Figure 5 shows that plots of the wave height in centimeters from the voltammograms versus the percentage of antioxidant give straight lines through the origin for all of the antioxidants of interest. As a result, if a single antioxidant is present in a lubricant and can be identified, its concentration can easily be determined from the standard curve generated in the electrochemical analysis.

Standard lubricant solutions containing two antioxidants were also analyzed by the electrochemical method. The analyses showed that PAN and PTZ were easily identifiable in binary mixtures containing either O-PAN or DODA. This is due to the fact that the half-wave potentials of PAN (0.69 V) and PTZ (0.41 V and 0.69 V) are widely separated from those of O-PAN and DODA



(0.59 V and 0.58 V, respectively) and that both PAN and PTZ show relatively high wave heights (limiting currents). The analyses also showed that, at high (>1%) antioxidant concentrations, it was possible to detect PAN in combination with PTZ by comparing the relative heights of the two waves generated in the voltammogram. The wave heights of O-PAN and DODA are substantially smaller than those of PAN and PTZ (roughly 1/2 and 1/4 that of PAN, respectively), however. These potential/current characteristics make it difficult to distinguish O-PAN and DODA from each other or from PAN or PTZ. In most cases, therefore, electrochemical analysis is currently incapable of determining whether one or two antioxidants are present in a lubricant. Some prior knowledge of the lubricant formulation is needed or the use of some complementary analytical technique (such as the spectrochemical method) is required to determine the number of antioxidants in a sample. Moreover, if two antioxidants are known to be present in a lubricant, their individual concentrations cannot, as yet, be determined by the electrochemical method. Upper and lower limits for the total antioxidant concentration are obtainable, however.

With the data collected on standard lubricant solutions, electrochemical analysis was carried out on the series of unstressed lubricants that were known to each contain two antioxidants. In this analysis, the presence or the absence of PAN and/or PTZ in a given lubricant was determined from the shape of the voltammogram and from the half-wave potentials measured.

If PAN were found in a lubricant, then O-PAN was assumed to be absent since it was known that the two antioxidants were not both present in the same lubricant. The presence or absence of DODA was determined by the process of elimination. With the exception of sample 5B, the antioxidant identifications made on the basis on the electrochemical analysis were in agreement with those obtained by spectrochemical analysis and with the formulations specified. Once the antioxidants were identified, the height(s) of the peak(s) in the voltammograms were measured and compared with the standard curves in an attempt to determine either the individual antioxidant concentrations or the combined antioxidant concentration. Unequivocal determinations of either were impossible, however. A lubricant sample containing both PAN and DODA antioxidants and giving a voltammogram peak 1.9 cm high, for example, might contain 0.5 percent PAN (0.9 cm) and 2.0 percent DODA (1.0 cm), 1.0 percent PAN (1.6 cm) and 1.0 percent DODA (0.5 cm), or other combinations of antioxidants.

Several of the stressed lubricants were also analyzed by the electrochemical method. These analyses indicated that some new chemical species dominated the lubricant mixtures since the half-wave potentials measured were different from those obtained on either the standard lubricant/antioxidant solutions or on the unstressed lubricant solutions. These species are probably dimers, oligomers and/or oxidation products of the original antioxidants. Since many, if not all, of these species are being oxidized at the electrode at potentials near those of the

original antioxidants, it is reasonable to assume that they are active antioxidants themselves (see references 2 & 12). In addition, electrochemical analyses has been performed on PAN-protected PETH after breakdown and only small (roughly 1/20 that of PAN), diffuse waveforms were observed. Thus, any "composite" waveform exhibited by stressed oils should be a measure of the remaining antioxidant reservoir which could be used to estimate remaining lifetime.

It should be noted that during the electrochemical analyses some filming of the electrode occasionally occurred. This results in rather diffuse waveforms whose limiting current plateaus can be hard to discern. Polishing the electrode with 2 micron alumina for approximately two minutes usually alleviates this problem. Another potential solution is to sweep the voltage towards negative potentials which should oxidize the film coating the electrode thus cleaning it. This procedure has not yet been tried.

The use of alternative solvents needs to be assessed. Since the limiting currents and the half-wave potentials can be influenced by the solvent, a different choice of solvent may increase limiting currents for the DODA and may possibly result in more disperse half-wave potentials among the different antioxidant species. This, especially in the case of the unstressed antioxidant mixtures, might allow separation of the half-wave curves so that individual antioxidants can be identified and quantified. Another benefit that might occur from

a change in solvent is a decrease in the potential health risks associated with performing the analytical procedure. The safe exposure limits to the solvent's vapor would be significantly higher than that of acetonitrile if, for example, acetone or ethyl alcohol were to be an effective solvent.

## CONCLUSIONS

Two simple, sensitive analytical techniques for determining aryl amine antioxidants in ester lubricants have been developed. A spectrochemical technique is capable of distinguishing PAN from O-PAN and DODA, overwhelmingly the most common antioxidants used in today's ester lubricants. Quantitative measures of the concentration of PAN and O-PAN approaching a few percent error are possible in simple binary antioxidant formulations but the analyses for DODA show higher errors. This is probably due to the low optical density of the colored adduct used to detect DODA. Higher sample volumes of oil (> 100 microliters) should improve the accuracy of the analysis for DODA. Binary combinations of PAN or O-PAN with PTZ are not amenable to PTZ analysis by the spectrochemical method. These binary antioxidant formulations appear to form mixed dimers (PAN-PTZ, O-PAN-PTZ) which interfere with the spectrochemical measurements. An electrochemical method for antioxidant analysis circumvents this problem. Microelectrodes immersed in acetonitrile solutions of the oils show different half-wave potentials for PAN and PTZ and

the limiting currents provide quantitative information. O-PAN and DODA exhibit nearly identical half-wave potentials which are close to that of PAN. Thus, distinguishing mixtures of these antioxidants will be difficult but a "composite" antioxidant concentration is obtainable. Limited analyses on stressed oils confirm the presence of antioxidant reaction products that appear to have antioxidant activity. A complete analysis of these complex mixtures of antioxidant species is probably not possible by all but the most sophisticated analytical methods. However, a measure of a "composite" antioxidant concentration which could be related to remaining lifetime seems possible. Further studies of the electrochemical response of stressed oils correlated with the time remaining before lubricant breakdown is necessary to develop such an approach.

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TABLE 1. SPECTROCHEMICAL MEASUREMENTS OF PAN/O-PAN ANTIOXIDANTS IN UNSTRESSED OILS

Sample	True % Antioxidant	% Antioxidant			
		1 Minute Measurement at 528 nm with 0.1% NBDB		10 Minute Measurement at 528 nm with 0.01% NBDB	
		$\bar{x} \pm \sigma n-1$	% Difference	$\bar{x} \pm \sigma n-1$	% Difference
1A PAN O-PAN	1.10 --	1.04 $\pm$ .05	5	1.08 $\pm$ 0	2
2A PAN O-PAN	1.00 --	0.63 $\pm$ .03	37	0.66 $\pm$ .01	34
3A PAN O-PAN	1.00 --	1.00 $\pm$ .05	4	0.97 $\pm$ .07	7
5B PAN O-PAN	-- 2.15	2.19 $\pm$ .30	2	1.95 $\pm$ .04	9
6B PAN O-PAN	-- 1.90	2.07 $\pm$ .13	9	2.01 $\pm$ .11	6
10D-2 PAN O-PAN	1.90 --	1.60 $\pm$ .50	16	1.84 $\pm$ .01	3
12E PAN O-PAN	1.10 --	1.02 $\pm$ .03	7	1.05 $\pm$ .05	5

TABLE 2. SPECTROCHEMICAL MEASUREMENTS OF DODA  
ANTIOXIDANT IN UNSTRESSED OILS

<u>Sample</u>	<u>True % Antioxidant</u>	<u>% Antioxidant</u>	
		<u>3 Minute Measurement at 725 nm with 0.1% NBDB x ± σn-1</u>	<u>% Difference</u>
1A	1.30	0.81 ± .20	38
2A	1.00	0.84 ± .16	16
3A	1.25	0.55 ± 0	56
5B	0.35	0.10 ± 0	71
6B	1.50	1.17 ± .16	22
9D	1.55	2.18 ± .04	41
10D-2	1.50	0.71 ± .04	53
11E	1.55	2.08 ± .06	34
12E	1.30	.84 ± .16	35

TABLE 3. SPECTROCHEMICAL MEASUREMENTS OF ANTIOXIDANTS IN USED OILS

<u>Sample</u>	<u>% Antioxidant</u>	
	<u>PAN/O-PAN</u> 1 Minute Measurement at 528 nm with 0.1% NBDB	<u>DODA</u> 3 Minute Measurement at 725 nm with 0.1% NBDB
13A	0.93	1.02
14A	0.19/0.30	1.24
15B	0.06/0.08	0.31
16B	0.03/0.04	1.22
17C	0.07/0.10	2.25
18C	0.02/0.03	1.41
19C	0.03/0.05	1.15
20C	0.07/0.11	2.50
21C	0.04/0.05	1.97
22C	0.05/0.08	1.49
23D	0.34/0.52	1.24
24D	0.19/0.30	1.21
25D	0.18/0.28	1.27

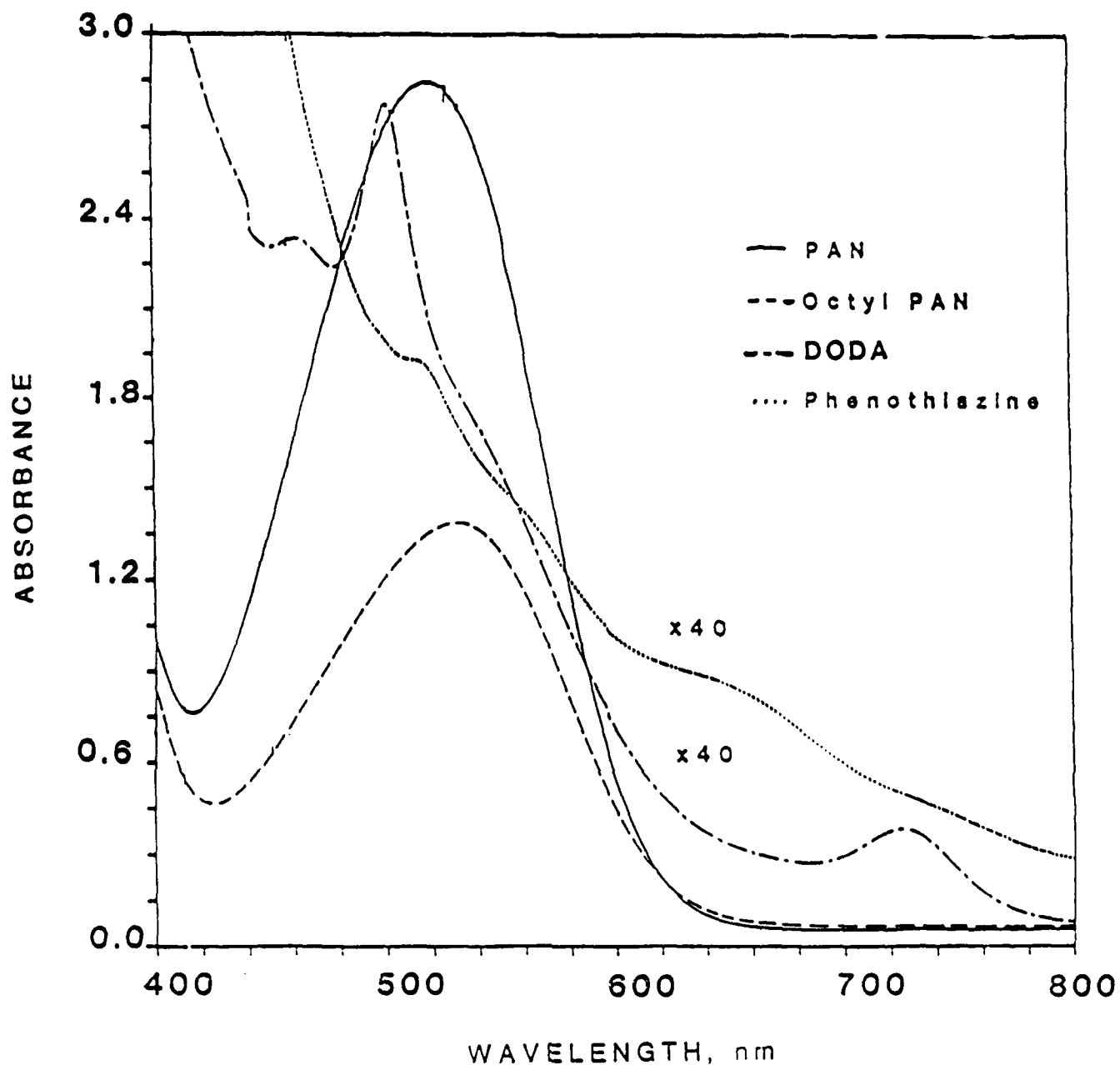


Figure 1. Visible absorption spectra of four aryl amine antioxidant/p-nitrobenzenediazonium tetrafluoroborate complexes.

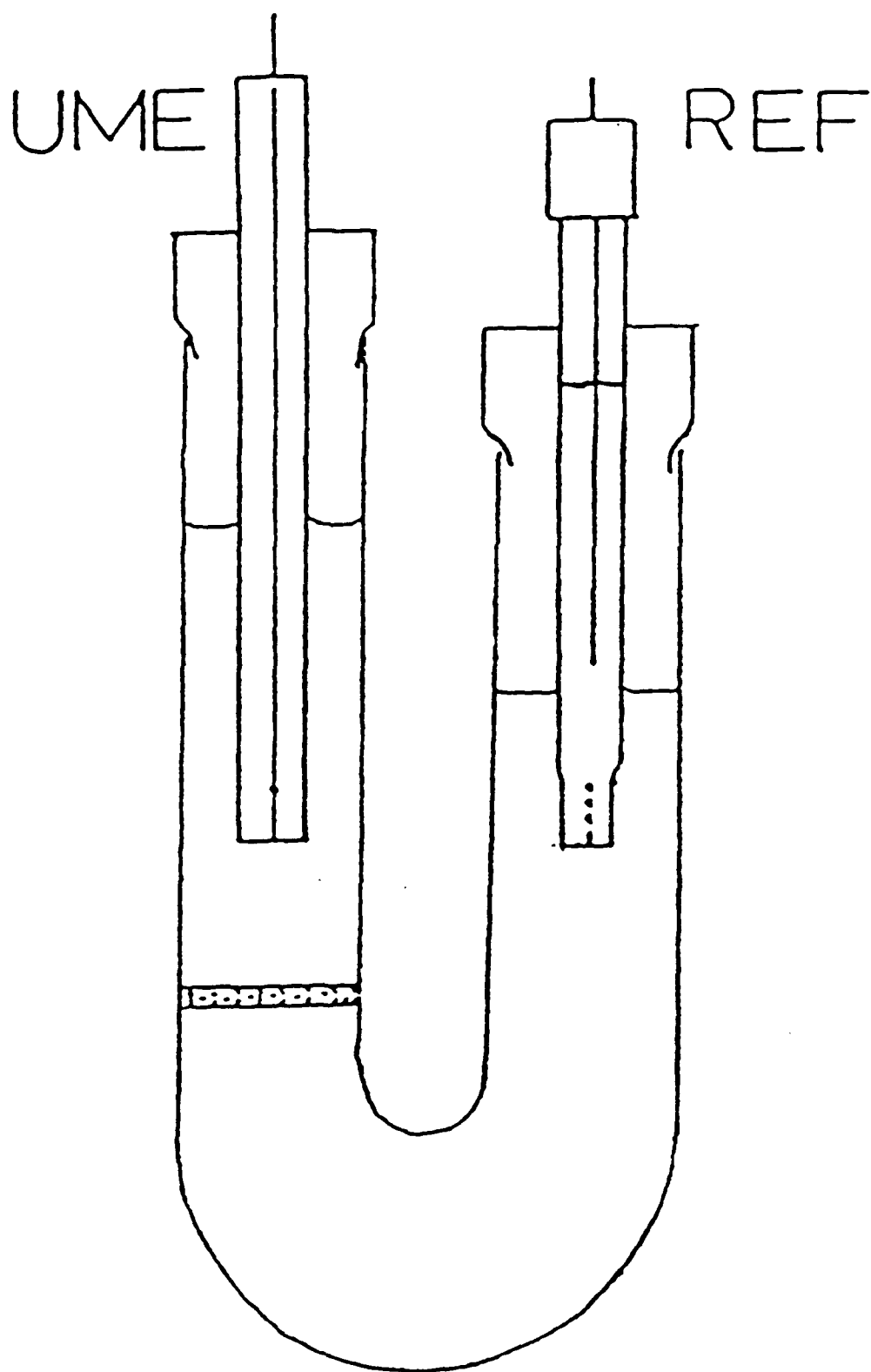


Figure 2. The electrochemical cell containing an ultramicroelectrode (UME) and a Ag/AgCl reference electrode (REF).

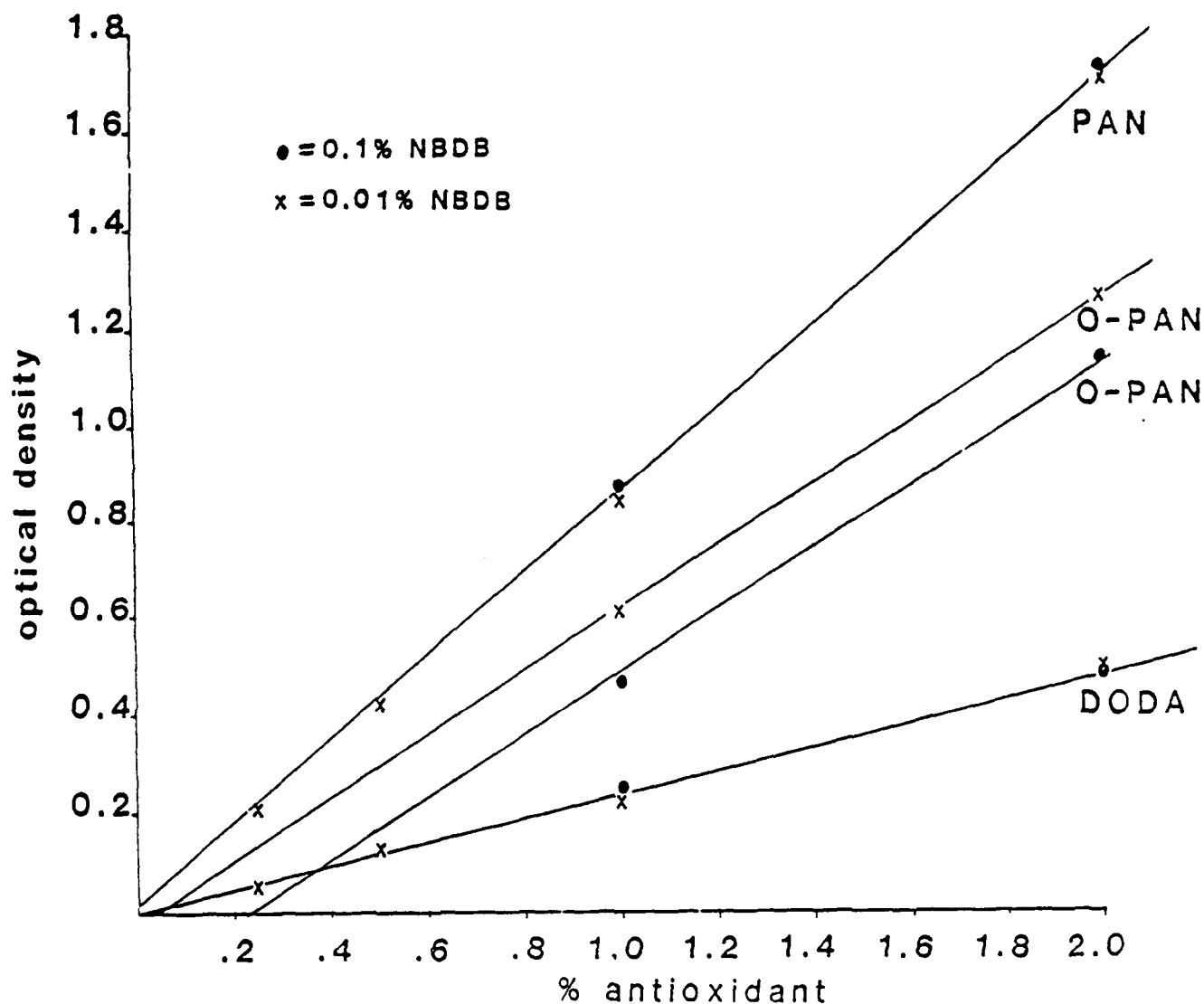


Figure 3. Plots of optical densities measured at the absorption wavelengths versus antioxidant concentration for standard solutions of three aryl amine antioxidants.

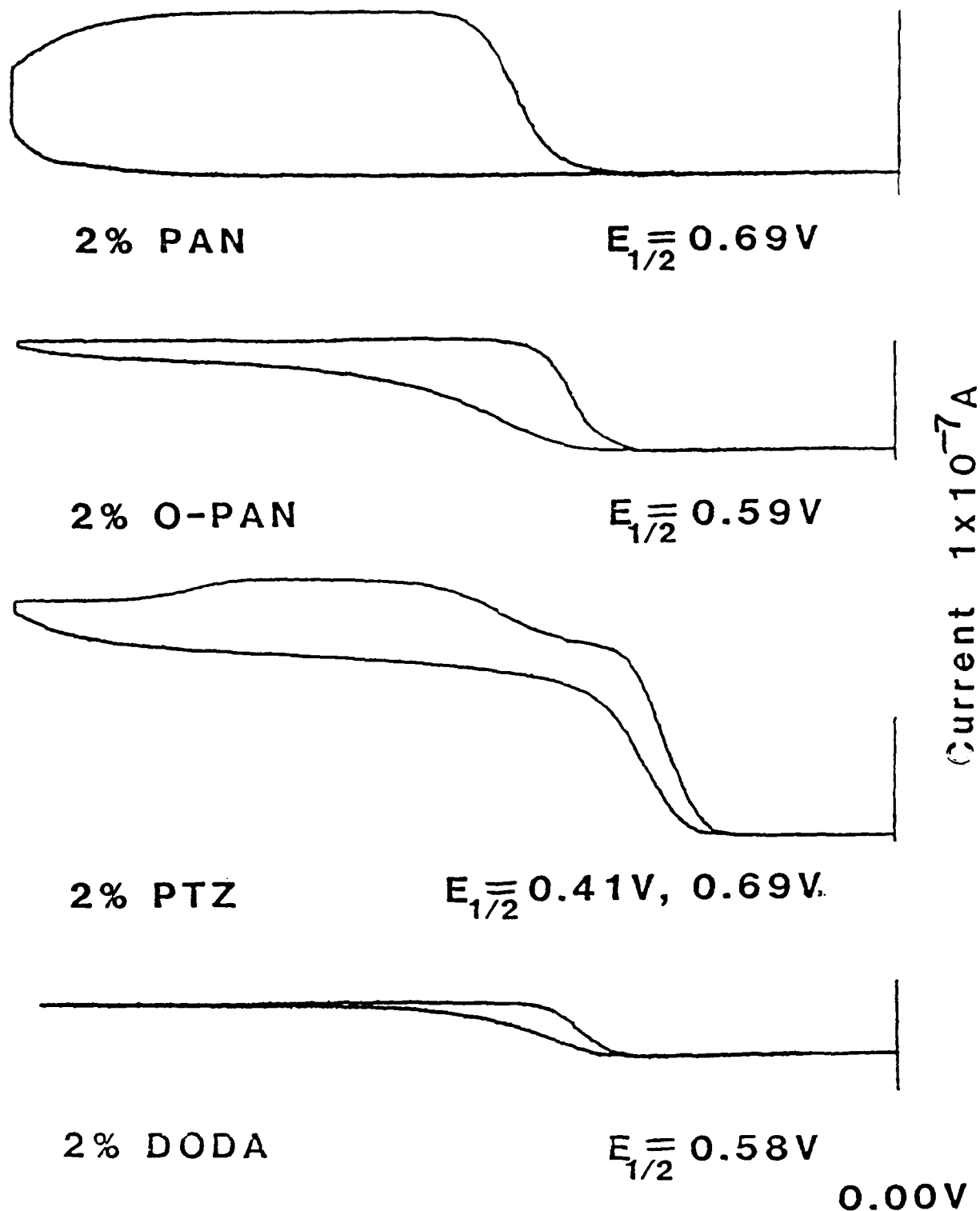


Figure 4. Cyclic voltammograms generated and half-wave potentials measured (versus Ag/AgCl reference electrode) for standard solutions of four aryl amine antioxidants.

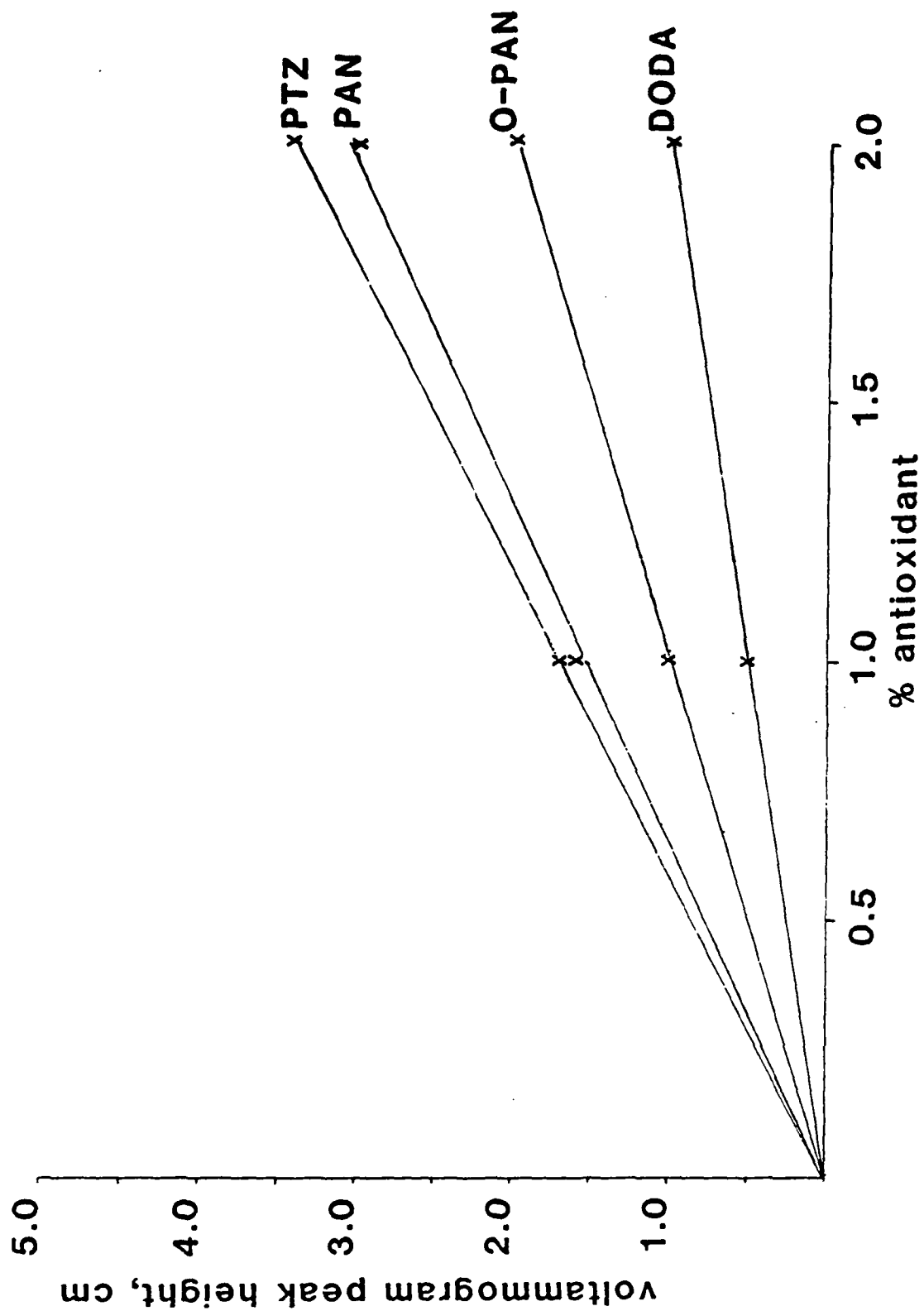


Figure 5. Plots of voltammogram peak height in centimeters versus antioxidant concentration for standard solutions of four aryl amine antioxidants.  
(Scale: 1 cm = 100 nA)